SPECIFICATION

METHOD OF ANALYZING MINUTE QUANTITY OF CONTENT

TECHNICAL FIELD

The present invention relates to methods of analyzing minute quantities of contents in materials, specifically relates to methods of analyzing minute quantities of contents such as additives included in polymer materials.

BACKGROUND ART

A flowchart is illustrated in Fig. 23 that represents a conventional method of analyzing additives included in polyolefin-group resin such as polypropylene (referred to as PP) and polyethylene (referred to as PE). First, the additives are extracted for 8 hours with a solvent such as chloroform heated up close to its boiling point, from pellets of the polyolefin-group resin as a sample (referred to as processing "A"). Here, this extraction is performed twice, and thus, all of the additives are extracted. Next, after chloroform is removed from the chloroform extract, the reflux extraction is performed for 1 hour using heated acetone (referred to as processing "B"); then, using this extract after acetone is removed, analysis is performed by either the liquid chromatography analyzer or the gas chromatography analyzer; consequently, the additives such as an antioxidant and a flame retardant are identified and quantified. On the other hand, regarding the residues remaining after the chloroform extraction, extraction is performed for 4 hours using heated N,N-dimethylformamide (referred to as processing "C"); then, the extract obtained is analyzed by the infrared spectrum analyzer, and thus, an additive such as a metal deactivator is identified.

In the processing "A", an acetone/toluene solvent mixture of 1:1 by volume ratio can also be used as the solvent other than chloroform. As a method for the processing "A", for example, the Soxhlet extraction method is used, in which this extraction is not limited to twice, but performed more than twice in response to necessity. Here, in the Soxhlet extraction method used for the processing "A",

because the extraction is performed with the solution being refluxed, a specified volume of the solution is needed; thus, as chloroform, for example, the volume of approximately 100 ml is needed. Therefore, the amount of approximately 10 g is used for the sample pellets. Additionally, in the processing "A", because the extraction is performed using the solvent heated up close to its boiling point, due to the resin of the base material being partially extracted, this causes interference in the analysis; therefore, by re-extracting the chloroform extract using acetone that can only extract the additives, the resin component as the interference in the analysis is removed. Here, in the processing "A", if a solvent that extracts only the additives is used, the extraction time becomes further long (for example, referred to as Non-Patent Document 1).

[Non-Patent Document 1]

Technical Information Institute, Ed., "Separation and Analysis Technology of Polymer Additives", on page 19 -21.

DISCLOSURE OF THE INVENTION

As described above, in the conventional method of analyzing the minute quantity of the content, although the step of analyzing the extract-processed content has not been needed for a long time because of using instrumental analysis, regarding the step of preparing the sample, because not only a plural number of extraction treatment using same methods needed for a long time is performed, but also a plurality of different methods is also performed, it has been needed for a remarkably long time; consequently, a problem has occurred in which the minute quantity of the content cannot be rapidly identified and quantified.

An objective of the present invention, which is made to solve the above described problem, is to provide a method of rapidly analyzing a minute quantity of a content included in a material, in which sample preparation when the minute quantity of the content included in the material is analyzed is performed by once short-time extraction treatment without a plural number of the extraction treatment taking a long time and a plurality of different extraction-treatment methods.

According to a first aspect of the present invention, a method of analyzing a minute quantity of content by analyzing extract extracted with a solvent from the content included in a material includes a step of mounting on a sample table a sample piece of the material to be analyzed; a step of dropping onto the sample table the solvent for extracting the content from the sample piece, and injecting the solvent into a gap between the sample table and the sample piece; a step of maintaining at room temperature the solvent injected into the gap between the sample table and the sample piece, and, with the solvent maintained in the gap between the sample table and the sample piece, extracting the content from the sample piece; and a step of analyzing the content extracted from the sample piece.

According to a second aspect of the present invention, a method of analyzing a minute quantity of content by analyzing extract extracted with a solvent from the content included in a material includes a step of mounting, in contact with the top face of a sample table, a sample piece of the material to be analyzed; a step of dropping onto the sample table the solvent for extracting the content from the sample piece, and injecting the solvent into a gap between the top face of the sample table and the sample piece mounted in contact with the top face of the sample table; a step of maintaining at room temperature the solvent injected into the gap between the top face of the sample table and the sample piece, and, with the solvent maintained in the gap between the top face of the sample table and the sample piece, extracting the content from the sample piece; and a step of analyzing the content extracted from the sample piece.

According to a third aspect of the present invention, in the method of analyzing the minute quantity of the content according to the second aspect, the step of analyzing the content extracted from the sample piece includes a chromatographic analyzing method of analyzing solution including the content extracted from the sample piece.

According to a forth aspect of the present invention, in the method of analyzing the minute quantity of the content according to the second aspect, the step of analyzing the content extracted from the sample piece includes a method of, after

removing by vaporization of the solvent in the solution including the content extracted from the sample piece so as to deposit the content onto the surface of a substrate used as the sample table, analyzing the content deposited on the surface of the substrate.

According to a fifth aspect of the present invention, the method of analyzing the minute quantity of the content according to the forth aspect, the method of analyzing the content deposited on the surface of the substrate is the time-of-flight secondary ion mass spectrometry method.

According to a sixth aspect of the present invention, in the method of analyzing the minute quantity of the content according to the second aspect, as the step of extracting the content from the sample piece, a method of extracting, by adding vibration in a state in which the solvent is maintained at room temperature in the gap between the top face of the sample table and the sample piece, using the solvent maintained in the gap between the top face of the sample table and the sample piece, the content from the sample piece is used.

According to a seventh aspect of the present invention, in the method of analyzing the minute quantity of the content according to the second aspect, as the step of extracting the content from the sample piece, a method of extracting, by maintaining the solvent in the gap between the top face of the sample table and the sample piece in the saturated vapor atmosphere, at room temperature, of the solvent used for the extraction, using the solvent maintained in the gap between the top face of the sample table and the sample piece, the content from the sample piece is used.

According to an eighth aspect of the present invention, in the method of analyzing the minute quantity of the content according to the fifth aspect, the solvent, maintained in the gap between the top face of the sample table and the sample piece, for extracting the content from the sample piece additionally includes a silver composition soluble in the solvent.

According to the first aspect of the present invention, the method of analyzing the minute quantity of the content by analyzing the extract extracted with the solvent from the content included in the material includes the step of mounting on the sample table the sample piece of the material to be analyzed; the step of dropping onto the

sample table the solvent for extracting the content from the sample piece, and injecting the solvent into the gap between the sample table and the sample piece; the step of maintaining at room temperature the solvent injected into the gap between the sample table and the sample piece, and, with the solvent maintained in the gap between the sample table and the sample piece, extracting the content from the sample piece; and the step of analyzing the content extracted from the sample piece; thereby, the extraction time can be shortened, and, using a small amount of the sample piece, accurate analysis of the content in the material can be performed in a short time.

According to the second aspect of the present invention, the method of analyzing the minute quantity of the content by analyzing the extract extracted with the solvent from the content included in the material includes the step of mounting, in contact with the top face of the sample table, the sample piece of the material to be analyzed; the step of dropping onto the sample table the solvent for extracting the content from the sample piece, and injecting the solvent into the gap between the top face of the sample table and the sample piece mounted in contact with the top face of the sample table; the step of maintaining at room temperature the solvent injected into the gap between the top face of the sample table and the sample piece, and, with the solvent maintained in the gap between the top face of the sample table and the sample piece, extracting the content from the sample piece; and the step of analyzing the content extracted from the sample piece; thereby, the extraction time can be shortened, and, using a small amount of the sample piece, accurate analysis of the content in polymer material can be performed in a short time.

According to the third aspect of the present invention, in the method of analyzing the minute quantity of the content according to the second aspect, the step of analyzing the content extracted from the sample piece includes the chromatographic analyzing method of analyzing the solution including the content extracted from the sample piece; thereby, the extraction time can be shortened, and, using a small amount of the sample piece, accurate analysis of the content in polymer material can be performed in a short time.

According to the forth aspect of the present invention, in the method of analyzing the minute quantity of the content according to the second aspect, the step of analyzing the content extracted from the sample piece includes the method of, after removing by vaporization of the solvent in the solution including the content extracted from the sample piece so as to deposit the content onto the surface of the substrate used as the sample table, analyzing the content deposited on the surface of the substrate; thereby, the extraction time can be shortened, and, using a small amount of the sample piece, accurate analysis of the content in polymer material can be performed in a short time.

According to the fifth aspect of the present invention, the method of analyzing the minute quantity of the content according to the forth aspect, the method of analyzing the content deposited on the surface of the substrate is the time-of-flight secondary ion mass spectrometry method; thereby, the extraction time can be shortened, and, using a small amount of the sample piece, accurate analysis of the content in polymer material can be performed in a short time. Especially, analysis of the minute quantity of the content becomes possible.

According to the sixth aspect of the present invention, in the method of analyzing the minute quantity of the content according to the second aspect, as the step of extracting the content from the sample piece, the method of extracting, by adding vibration in the state in which the solvent is maintained at room temperature in the gap between the top face of the sample table and the sample piece, using the solvent maintained in the gap between the top face of the sample table and the sample piece, the content from the sample piece is used; thereby, the extraction time can be shortened, and, using a small amount of the sample piece, accurate analysis of the content in polymer material can be performed in a short time. Especially, because the amount of the extract from the sample piece increases, the analysis accuracy of the extract improves.

According to the seventh aspect of the present invention, in the method of analyzing the minute quantity of the content according to the second aspect, as the step of extracting the content from the sample piece, the method of extracting, by

maintaining the solvent in the gap between the top face of the sample table and the sample piece in the saturated vapor atmosphere, at room temperature, of the solvent used for the extraction, using the solvent maintained in the gap between the top face of the sample table and the sample piece, the content from the sample piece is used; thereby, the extraction time can be shortened, and, using a small amount of the sample piece, accurate analysis of the content in polymer material can be performed in a short time. Especially, because the re-dropping of the solvent used for the extraction becomes unnecessary, the analysis process becomes simple.

According to the eighth aspect of the present invention, in the method of analyzing the minute quantity of the content according to the fifth aspect, the solvent, maintained in the gap between the top face of the sample table and the sample piece, for extracting the content from the sample piece additionally includes the silver composition soluble in the solvent; thereby, the extraction time can be shortened, and, using a small amount of the sample piece, accurate analysis of the content in polymer material can be performed in a short time. Especially, the sensitivity, using the time-of-flight secondary ion mass spectrometry method, for analyzing the extract from the material is remarkably improved.

BRIEF DESCRIPTION OF DRAWINGS

Fig. 1 is a flow chart explaining a method of analyzing a minute quantity of a content included in a material according to the present invention;

Fig. 2 is views illustrating states in which an extraction solvent is dropped, according to the analyzing method of the present invention;

Fig. 3 is a view illustrating a state, according to the analyzing method of the present invention, in which a sample piece is mounted in contact with the top face of a sample table, and the extraction solvent is maintained in gaps between the top face of the sample table and the sample piece;

Fig. 4 is views representing a first method, of preparing a specimen, for analyzing extract by an analyzer, according to an analyzing method of the present invention;

Fig. 5 is views illustrating a second method, of preparing a specimen, for analyzing extract by an analyzer, according to an analyzing method of the present invention;

Fig. 6 is, as an example of the measurement results according to Example 1, a chromatogram of extraction solution extracted from an HDPE pellet including an antioxidant of 500 ppm;

Fig. 7 is a graph representing a relationship between areas of the peaks "A" obtained from the chromatograms in which the extraction solutions extracted from the HDPE pellets each including the antioxidant of 50 ppm, 100 ppm, 500 ppm, or 1000 ppm as the concentration, and the antioxidant concentrations, according to Example 1;

Fig. 8 is, as an example of the measurement results according to Example 2, an infrared absorption spectrum of extract extracted from a PP pellet including a brominated flame retardant of 0.1%;

Fig. 9 is a graph representing a relationship between the absorbance values of the infrared absorption peaks obtained from the analysis in which the extracts are extracted from the PP pellets each including the brominated flame retardant of 0.1%, 1%, or 10% as the concentration, and the brominated flame-retardant concentrations, according to Example 2;

Fig. 10 is, as an example of the measurement results according to Example 3, a photoelectron spectrum of extract extracted from the PP pellet including the brominated flame retardant of 0.1%;

Fig. 11 is a graph representing a relationship between the peak areas at close to 69 eV of the photoelectron spectra obtained from the analysis in which the extracts are extracted from the PP pellets each including the brominated flame retardant of 0.1%, 1%, or 10% as the concentration, and the brominated flame-retardant concentrations, according to Example 3;

Fig. 12 is, as an example of the measurement results according to Example 4, a mass spectrum of extract extracted from the HDPE pellet including the antioxidant of 500 ppm;

Fig. 13 is a graph representing a relationship between the mass-spectrum

peak-area ratios ($^{775}M^{+}/^{28}Si^{+}$) obtained from the analysis in which the extracts are extracted from the HDPE pellets each including the antioxidant of 10 ppm, 50 ppm, 100 ppm, 500 ppm, or 1000 ppm as the concentration, and the antioxidant concentrations, according to Example 4;

Fig. 14 is, as an example of the measurement results according to Example 5, a mass spectrum of extract extracted from a PP pellet including the brominated flame retardant of 100 ppm;

Fig. 15 is a graph representing a relationship between the mass-spectrum peak-area ratios ($^{79}Br^{-}/^{107}Ag^{-}$) obtained from the analysis in which the extracts are extracted from the PP pellets each including the brominated flame retardant of 1 ppm, 10 ppm, 100 ppm, 1000 ppm, 1%, or 10% as the concentration, and the brominated flame retardant concentrations, according to Example 5;

Fig. 16 is, as an example of the measurement results according to Example 6, a mass spectrum of extract extracted from an HIPS pellet including the brominated flame retardant of 0.1%;

Fig. 17 is a graph representing a relationship between the mass-spectrum peak-area ratios ($^{1068}(B+Ag)^{+}/^{107}Ag^{+}$) obtained from the analysis in which the extracts are extracted from the HIPS pellets each including the brominated flame retardant of 0.1%, 1%, or 10% as the concentration, and the brominated flame retardant concentrations, according to Example 6;

Fig. 18 is a view representing a state in which content is extracted from a sample piece according to Example 7;

Fig. 19 is a mass spectrum of the extract, obtained by the method according to Example 7, extracted from the HDPE pellet including the antioxidant of 500 ppm;

Fig.20 is a view representing a state according to Example 8, in which a content is extracted from a sample piece;

Fig. 21 is a mass spectrum of the extract, obtained by the method according to Example 8, extracted from the PP pellet including the brominated flame retardant of 100 ppm;

Fig. 22 is a mass spectrum of extract, obtained by a method according to

Example 9, extracted from the HIPS pellet including the brominated flame retardant of 0.1%; and

Fig. 23 is a flowchart representing a conventional method of analyzing an additive included in polyolefin-group resin.

BEST MODE FOR CARRYING OUT THE INVENTION

Fig. 1 is a flow chart explaining a method of analyzing a minute quantity of a content included in a material according to the present invention. In a first step, a sample piece 1 of the material including a substance to be analyzed is mounted in contact with the top face of a sample table 2 (Fig. 1(a)). In a second step, a solvent 3 for extracting the content from the sample piece 1 is dropped onto the top face of the sample table 2 so as to inject the solvent into the gaps between the top face of the sample table 2 and the sample piece 1 (hereinafter referred to as "gaps between the sample table 2 and the sample piece 1") (Fig. 1(b)). In a third step, the solvent 3 injected into the gaps between the sample table 2 and the sample piece 1 is kept for a short time at room temperature; thus, by the solvent 3 maintained in the gaps between the sample table 2 and the sample piece 1, the content to be analyzed is extracted from the sample piece 1 (Fig. 1(c)). In a forth step, the content extracted from the sample piece 1 is analyzed by an instrumental analyzer 10 (Fig. 1(d)).

In the analyzing method according to the present invention, as the material to be analyzed, polymer materials such as plastic, rubber, adhesives, encapsulating resin, and mold resin are listed. These polymer materials are analyzed not only in the state of the materials themselves, but also in a state in which the materials are used in instrumental parts such as an instrumental case, a molded product, and a printed wiring board. In the analyzing method according to the present invention, as materials to be analyzed, a sub-material such as an antioxidant, a fire retardant, a curing catalyst, or a processing aid included in a polymer material, as well as a minute quantity of a substance that may be included either during the material itself being produced, or during the material being molded/processed into various parts of a product can be listed; however, if the substance that can be extracted with a solvent

from the polymer material to be applied is used, the material is not limited to the above. In the analyzing method according to the present invention, a little amount of the sample piece such as an approximately one resin-pellet amount (for example, 0.1 - 0.5 g in weight) may also be used.

In the analyzing method according to the present invention, as the sample table for mounting the sample piece, any table having a flat face that can mount the sample piece may be applied, and especially, a substrate is preferably applied. As the materials of the sample table, a glass material, an inorganic material, a metallic material, and a plastic material having chemical resistance, etc. that do not include the substance to be analyzed, are listed. When the liquid chromatography method, the gas chromatography method, or the liquid-chromatography/mass-spectrometry method is applied as the analyzing method, specifically, for example, a glass substrate, a silicon substrate, a germanium substrate, a silver substrate, a gold substrate, a poly(tetrafluoroethylene) substrate, an SUS substrate on which poly(tetrafluoroethylene) is coated, a glass Petri dish, a silver container, a gold container, or a poly(tetrafluoroethylene) container is used as the table. When the infrared spectrum analysis is applied as the analyzing method, specifically, for example, a silicon substrate, a germanium substrate, or an SUS substrate on which poly(tetrafluoroethylene) is coated is used. Moreover, when the X-ray photoelectron spectroscopy method is applied as the analyzing method, a silicon substrate is used. Furthermore, when the time-of-flight secondary ion mass spectrometry method is applied as the analyzing method, for example, a silicon substrate, a germanium substrate, a silver substrate, a gold substrate, or an SUS substrate on which silver or gold is plated is used.

Fig. 2 is views illustrating states in which the extraction solvent is dropped, according to the analyzing method of the present invention. As represented in Fig. 2, the extraction solvent 3 is dropped using a microsyringe 4 onto the top face of the sample table 2 with which the pellet of the sample piece 1 is mounted in contact. In Fig. 2, a substrate as the sample tables 2 is represented as an example; hereinafter, a substrate 2 is explained as the sample table 2. However, according to the present

invention, the sample table 2 is not limited to the substrate. Regarding the dropping volume of the extraction solvent 3, the volume may be from a volume that can at least fill the gaps between the substrate 2 and the sample piece 1 to a volume that is twice the volume of the sample piece; thereby, for example, when the sample piece 1 is a single resin-pellet, the volume is 5 - 100 μl. Moreover, if the position to be dropped is on the top face of the substrate 2, the position is not especially limited; however, it is preferable to drop the solvent at a position, on the top face of the substrate 2, close to a portion on which the sample piece 1 is mounted, specifically, to drop at the boundary between the portion on which the sample piece 1 is mounted and the portion on which the sample piece 1 is not mounted, because the solvent 3 can be effectively injected into the gaps between the substrate 2 and the sample piece 1.

Fig. 3 is a view illustrating a state in which the sample piece 1 is mounted in contact with the top face of the substrate as the sample table 2. As represented in Fig. 3, the sample piece 1 has recesses and protrusions on its face contacting to the substrate 2; thereby, these protrusions contact to the top face of the substrate 2, meanwhile these recesses form gaps 9 between the substrate 2 and the sample piece 2, and thus, the solvent dropped is injected into the gaps 9. In the extraction of the content from the sample piece 1 according to the analyzing method of the present invention, the state in which the solvent 3 is at least maintained in the gaps 9 between the substrate 2 and the sample piece 1 is held at room temperature for a short time; thereby, the content is extracted into the solvent 3 contacting to the sample piece, especially into the solvent 3 existing in the gaps between the substrate 2 and the sample piece 1. At this time, because the solvent decreases due to its vaporization, after a predetermined time passes, the solvent 3 may be dropped again. For example, if the sample piece 1 is the single resin-pellet, the extraction time, that is, the time during the state in which the solvent 3 is maintained in the gaps between the substrate 2 and the sample piece 1 being held, and the content being extracted is preferably set for 0.5 - 30 minutes, and further preferably set for 0.5 - 15 minutes. If this time is shorter than 0.5 minutes, the extraction becomes insufficient; thereby, the analysis accuracy deteriorates. On the other hand, if the time is longer than 30

minutes, the repeating number of the dropping only increases without increase of the extract amount; thereby, not only the analysis process becomes more complex, but also the analysis time becomes longer.

Moreover, in order to increase the amount of the content extracted from the sample piece 1 into the solvent 3, the substrate 2 may be vibrated during the extraction. As the vibration method, a method of using an ultrasonic washer or a shaker, and a method in which an ultrasonic oscillator is pasted onto the substrate 2 are listed. Furthermore, by putting into a sealed container the substrate 2, the sample piece 1, and the solvent 3 maintained in the gaps between the substrate 2 and the sample piece 1, the extraction of the content may be performed from the sample piece 1 using the extraction solvent 3, in the saturated vapor atmosphere of the same solvent as the extraction solvent 3. According to this operation, loss of the extraction solvent 3 due to the vaporization is prevented, and additional dropping of the solvent becomes needless; consequently, the analyzing process can be simplified.

Fig. 4 is views representing a first method, of preparing a specimen, for analyzing the extract by an analyzer, according to an analyzing method of the present invention. This first method is especially used when the extract is analyzed by a chromatographic analyzing method such as the liquid chromatography method, the gas chromatography method, or the liquid-chromatography/mass-spectrometry method. As represented in Fig. 4, after the extraction step has finished, the test piece 1 is removed from the substrate 2; then, solution 5 including the extract placed on the top face of the substrate 2 is sampled using a microsyringe 6 into a sample cell 7. Then, this sampled solution 5 is injected into the analyzer, and the content included in the polymer material is analyzed.

Fig. 5 is views illustrating a second method, of preparing a specimen, for analyzing the extract by an analyzer, according to an analyzing method of the present invention. This second method is used when the extract is analyzed by any one of the X-ray fluorescence spectrometry method, the time-of-flight secondary ion mass spectrometry method, the infrared spectrometry method, and the X-ray photoelectron spectroscopy method. As represented in Fig. 5, after the extraction step has finished,

the test piece 1 is removed from the substrate 2, and then, the solvent of the solution 5 including the extract placed on the top face of the substrate 2 is removed by vaporization; thus, the substrate surface on which extract 8 is deposited is directly analyzed by the analyzer. In the analyzing method of the present invention, especially, when the extract is analyzed using the time-of-flight secondary ion mass spectrometry method, because if the extract exists too much, the deposition portion is charged up; therefore, in order to prevent the charging up, it is preferable that a silver substrate, a gold substrate, or an SUS substrate on which silver or gold is plated is used as the substrate. In the analyzing method of the present invention, as the solvent used for extracting, a solvent is used that extracts the content without decomposing the polymer material at room temperature. Regarding the grade of the solvent used, a solvent having the analysis grade purity is preferably used because of little influence on analyzing the content.

In the analyzing method of the present invention, especially, when the extract is analyzed using the time-of-flight secondary ion mass spectrometry method, the content is resolved in a solvent for extraction, and, if the solution is used in which a silver compound that does not include as an impurity the substance to be measured is added, not only the charging up can be prevented even if a chargeable substrate is used, but also the analysis sensitivity is improved; consequently, the analysis accuracy is improved. In the analyzing method of the present invention, the sample piece is mounted in contact with the top face of the sample table such as the substrate, the solvent is injected by dropping into the gaps between the sample table and the sample piece, the solvent injected is maintained in the gaps between the sample table and the sample piece, the content is extracted with this maintained solvent, and the extract is analyzed by the analyzer; therefore, the extraction time can be shortened, and using a small amount of the sample piece, accurate analysis of the content in the material, especially in the polymer material, can be performed in a short time. Hereinafter, more specific examples according to the present invention are represented; however, the present invention is not limited to these examples.

EXAMPLES

Example 1.

High density polyethylene (hereinafter referred to as HDPE) specimens each including an antioxidant of 50 ppm, 100 ppm, or 1000 ppm by weight were prepared. HJ340™ (produced by Japan Polychem Corp.) was used as HDPE, and 1,3,5-trimethyl-2,4,6 tris(3,5-di-tert-buthyl-4-hydroxybenzyl)benzene (Irganox 1330™, produced by Aldrich Corp.) was used as the antioxidant. As the sample piece 1, the antioxidant was added to and kneaded with the HDPE so that the concentration becomes above each value; thus, pellets were prepared in which the size of the single pellet is 5 mm × 3 mm × 3mm, and the weight is approximately 0.2 g. Similarly to the method represented in Fig. 2, the single HDPE pellet as the sample piece 1 was mounted in contact with a silicon substrate as the sample table 2, and 20 μl chloroform as the extraction solvent 3 was dropped using the microcyringe 4 so that the chloroform is injected into the gaps between the HDPE pellet and the silicon substrate; then, the sample piece was kept. Chloroform is a solvent that does not dissolve the HDPE, but dissolves the above antioxidant. The sample was kept at room temperature for 10 minutes after the dropping operation; however, because the volume of the chloroform decreases during the maintaining due to the vaporization, 20 μl chloroform was additionally dropped for every two minutes. The chloroform used was the liquid chromatography grade one (produced by Wako Pure Chemical Industries, Ltd.).

Similarly to the method represented in Fig. 4, after the sample was kept for 10 minutes, the HDPE pellet as the sample piece 1 was removed from the silicon substrate as the sample table 2. Next, the chloroform solution as the solution 5 including extract remaining on the top face of the silicon substrate was transferred into the sample cell 7 using the microcyringe 6, and then, adjusted to a constant volume of 50 μl. The time required from the start to now was 12 minutes. The solution in this sample cell 7 was injected into the liquid-chromatography/mass-spectrometry analyzer, and thus, the amount of the antioxidant was measured. Model HP8900™ (manufactured by Agilent Technologies

Inc.) was used as the liquid chromatography, Model LC-mate™ (manufactured by JEOL Ltd.) was used as the mass spectrometry, and Inertsil ODS-3™ (manufactured by GL Sciences Inc.) having the column inner diameter of 4.6 mm and the length of 150 mm was used as a column for separating organic compounds. Regarding the measurement condition of the liquid chromatography, the gradient mode using methanol and water as the eluent was applied, and the flow rate was set at 1 ml/minute. Regarding the measurement condition of the mass spectrometry, the atmospheric pressure chemical ionization method was used as an ionization method, the positive-ion mode was used, and the mass-to-charge ratio (referred to as "m/z") that is the ratio of the fragment mass number "m" to the charge "z" was set to 1 - 1000 as the measurement range; thus, the scanning measurement was performed.

Fig. 6 is, as an example of the measurement results, a chromatogram of the extraction solution extracted from the HDPE pellet including the antioxidant of 500 ppm. The peak "A" represents the separated peak of the antioxidant, while the peak "B" represents a silane coupling agent included in the pellet. Identification of these peaks was confirmed by checking the mass spectrum and the retention times of the chromatogram based on the measurement of the standard sample using corresponding substances. The peak area of the peak "A" was 5000 counts. Fig. 7 is a graph representing a relationship between areas of the peaks "A" obtained from the chromatograms in which the extraction solutions extracted from the HDPE pellets each including the antioxidant of 50 ppm, 100 ppm, 500 ppm, or 1000 ppm as the concentration, and the antioxidant concentrations. An excellent linear relationship was obtained between the antioxidant concentrations and the areas of the peaks "A" obtained from the chromatograms. In this example, the processing time was 12 minutes for extracting the antioxidant as the content from the HDPE pellet; thereby, it was found that the quantitative analysis of the antioxidant as the content can be performed by short-time extraction treatment. As described above, in the analyzing method according to this example, the extraction processing time can be considerably shortened compared to that in the conventional method, and the antioxidant as the content included in the HDPE specimen can be rapidly analyzed.

Example 2.

PP specimens each including as an additive a brominated flame retardant of 0.1%, 1%, or 10% by weight were prepared as samples. PC03B™ (produced by Japan Polychem Corp.) was used as PP, and decabromodiphenylether (produced by Wako Pure Chemical Industries, Ltd.) was used as the brominated flame retardant. As the sample piece 1, the brominated flame retardant was added to and kneaded with the PP so that the concentration becomes above each value; thus, pellets were prepared in which the size of the single pellet is 5 mm × 3 mm × 3mm, and the weight is approximately 0.2 g. Similarly to the method represented in Fig. 2, the single PP pellet as the sample piece 1 was mounted in contact with an SUS substrate coated with fluororesin as the sample table 2, and 20 μl toluene as the extraction solvent 3 was dropped using the microcyringe 4 so that the toluene is injected into the gaps between the PP pellet and the SUS substrate coated with fluororesin; then, the sample piece was kept. Toluene is a solvent that does not dissolve PP, but dissolves the above brominated flame retardant. The sample was kept at room temperature for 10 minutes after the dropping operation; however, because the volume of the toluene decreases during the maintaining due to the vaporization, 20 μl toluene was additionally dropped after five minutes. The toluene used was the liquid chromatography grade one (produced by Wako Pure Chemical Industries, Ltd.). Because after 10 minutes from the first toluene drop, the dropped toluene had been removed by vaporization, the PP pellet and the substrate were in a dry state. Then, when the PP pellet was removed from the substrate, similarly to the case represented in Fig. 5, extract from the pellet was deposited on the surface of the substrate as a condensed substance.

This deposited substance on the surface of the substrate was analyzed by the microscopic Fourier-transform infrared spectroscopic method. Model JIR-5500™ (manufactured by JEOL Ltd.) was used as the microscopic Fourier-transform infrared spectrometer. Regarding the measurement condition, the reflection mode was used, in which the measurement wavenumber range was set to 700 - 4000 cm^{-1}, and the

wavenumber resolution was set at 2 cm^{-1}. Fig. 8 is, as an example of the measurement results, an infrared absorption spectrum of the extract extracted from the PP pellet including the brominated flame retardant of 0.1%. As represented in Fig. 8, the infrared absorption peak caused by decabromodiphenylether was observed close to 1300 cm^{-1}. Fig. 9 is a graph representing a relationship between the absorbance values of the infrared absorption peaks obtained from the analysis in which the extract is extracted from the PP pellets each including the brominated flame retardant of 0.1%, 1%, or 10% as the concentration, and the brominated flame-retardant concentrations. An excellent linear relationship was obtained between the brominated flame-retardant concentrations and the absorbance values of the infrared absorption peaks. In this example, the processing time was 10 minutes for extracting the brominated flame retardant as the content from the PP pellet; thereby, it was found that the quantitative analysis of the brominated flame retardant as the content can be performed by short-time extraction treatment. As described above, in the analyzing method according to this example, the extraction processing time can be considerably shortened compared to that in the conventional method, and the brominated flame retardant as the content included in the PP specimen can be rapidly analyzed.

Example 3.

Except for a silicon substrate being used as the substrate to be the sample table 2, similarly to the procedure in Example 2, the drop operation using the extraction solvent, the extraction operation, and the deposition/fixation operation of the extract were performed. In this example, the deposited substance on the surface of the substrate was analyzed by the X-ray photoelectron spectroscopy method. Model QUANTUM2000™ (manufactured by Physical Electronics Industries Inc.) was used as the X-ray photoelectron spectroscopic analyzer, and the measurement range was set to 60 · 80 eV. Fig. 10 is, as an example of the measurement results, a photoelectron spectrum of the extract extracted from the PP pellet including the brominated flame retardant of 0.1%. As represented in Fig. 10, the photoelectron

spectrum caused by the $3d_{3/2}$ and $3d_{5/2}$ orbits of bromine included in decabromodiphenylether was observed close to 69 eV, and the spectrum peak area was 20. Fig. 11 is a graph representing a relationship between the peak areas at 69 eV of the photoelectron spectra obtained from the analysis in which the extract is extracted from the PP pellets each including the brominated flame retardant of 0.1%, 1%, or 10% as the concentration, and the brominated flame-retardant concentrations. An excellent linear relationship was obtained between the brominated flame-retardant concentrations and the peak area. In this example, the processing time was 10 minutes for extracting the brominated flame retardant as the content from the PP pellet; thereby, it was also found that the quantitative analysis of the brominated flame retardant as the content can be performed by a short-time extraction operation. As described above, in the analyzing method according to this example, the extraction processing time can also be considerably shortened compared to that in the conventional method, and the brominated flame retardant as the content included in the PP specimen can be rapidly analyzed.

Example 4.

Except for HDPE pellets each including the antioxidant of 10 ppm, 50 ppm, 100 ppm, 500 ppm, or 1000 ppm by weight being prepared as the sample pieces1, similarly to the procedure in Example 1, the drop operation using the extraction solvent, and the extraction operation were performed. In this example, after ten minutes passed from the first dropping of chloroform, the HDPE pellet was removed from the top face of the substrate without dropping chloroform again. Next, the substrate was kept for two minutes at room temperature so that the chloroform is removed by vaporization; thus, extract from the pellet was deposited as a condensed substance on the surface of the substrate. In this example, the deposited substance on the surface of the substrate was analyzed by the time-of-flight secondary ion mass spectrometry method. TRIFT2™ (manufactured by ULVAC-PHI Inc.) was used as the time-of-flight secondary ion mass spectrometry analyzer. Regarding the measurement condition, $^{69}Ga^{+}$ ion was used as the primary ion, the measurement

mode of the secondary ion was set to the positive ion mode, the measurement range was set to m/z = 1 · 1000, and the mass resolution was set to approximately $\Delta M/M$ = 5000.

Fig. 12 is, as an example of the measurement results, a mass spectrum of the extract extracted from the HDPE pellet including the antioxidant of 500 ppm. As represented in Fig. 12, the mass peak caused by the fragment of the antioxidant was observed at m/z = 775. Quantitative analysis was performed using the normalized ($^{775}M^+/^{28}Si^+$) area ratio in which the area of the peak at m/z = 775 ($^{775}M^+$) is normalized by the area of the peak at m/z = 28 ($^{28}Si^+$) caused by the fragment of silicon included in the substrate. The area ratio of the extract extracted from the HDPE pellet including the antioxidant of 500 ppm was 5. Fig. 13 is a graph representing a relationship between the mass-spectrum peak-area ratios ($^{775}M^+/^{28}Si^+$) obtained from the analysis of the extracts extracted from the HDPE pellets each including the antioxidant of 10 ppm, 50 ppm, 100 ppm, 500 ppm, or 1000 ppm as the concentration, and the antioxidant concentrations. An excellent linear relationship was obtained between the antioxidant concentrations and the peak-area ratios ($^{775}M^+/^{28}Si^+$), and especially, it was found to be also detectable at the minute concentration of 10 ppm. In this example, the processing time was 12 minutes for extracting the antioxidant as the content from the HDPE pellet; thereby, it was found that the quantitative analysis, also up to such minute concentration, of the antioxidant as the content can be performed by a short-time extraction operation. As described above, in the analyzing method according to this example, the extraction processing time can also be considerably shortened compared to that in the conventional method, and the antioxidant minutely included, for example, 10 ppm, in the HDPE specimen can be rapidly analyzed.

Example 5.

Similarly to the method in Example 2, PP pellets each including the brominated flame retardant of 1 ppm, 10 ppm, 100 ppm, 1000 ppm, 1%, or 10% by weight concentration were prepared as the sample pieces 1. Next, except for a silver

substrate being used for a substrate as the sample table 2, similarly to the procedure in Example 2, extract from each PP pellet was deposited as a condensed substance on the surface of the substrate. In this example, the deposited substance on the surface of the substrate was analyzed by the time-of-flight secondary ion mass spectrometry method. TRIFT2™ (manufactured by ULVAC-PHI Inc.) was used as the time-of-flight secondary ion mass spectrometry analyzer. Regarding the measurement condition, $^{69}Ga^{+}$ ion was used as the primary ion, the measurement mode of the secondary ion was set to the negative ion mode, the measurement range was set to m/z = 1 - 200, and the mass resolution was set to approximately $\Delta M/M$ = 5000. Fig. 14 is, as an example of the measurement results, a mass spectrum of the extract extracted from the PP pellet including the brominated flame retardant of 100 ppm. As represented in Fig. 14, the mass-spectrum peak caused by the fragment of the bromine element was observed at m/z = 79. Quantitative analysis was performed using the normalized ($^{79}Br^{-}/^{107}Ag^{-}$) peak-area ratio in which the area of the peak at m/z = 79 ($^{79}Br^{-}$) is normalized by the area of the peak at m/z = 107 ($^{107}Ag^{-}$) caused by the fragment of silver in the substrate.

Fig. 15 is a graph representing a relationship between the mass-spectrum peak-area ratios ($^{79}Br^{-}/^{107}Ag^{-}$) obtained from the analysis of the extracts extracted from the PP pellets each including the brominated flame retardant of 1 ppm, 10 ppm, 100 ppm, 1000 ppm, 1%, or 10% as the concentration, and the brominated flame retardant concentrations. An excellent linear relationship was obtained between the brominated flame retardant concentrations and the peak-area ratios, and especially, it was found to be also detectable at the minute concentration of 1 ppm. In this example, the processing time was 10 minutes for extracting the brominated flame retardant as the content from the PP pellet of the sample piece 1; thereby, it was found that the quantitative analysis, also up to such minute concentration, of the brominated flame retardant as the content can be performed by a short-time extraction operation. As described above, in the analyzing method according to this example, the extraction processing time can also be considerably shortened compared to that in the conventional method, and the brominated flame retardant minutely

included, for example, 1 ppm, in the PP specimen can be rapidly analyzed.

Example 6.

High impact polystyrene (referred to as HIPS) specimens each including brominated flame retardant as the additive of 0.1%, 1%, or 10% by weight were prepared as the samples. H8672™ (produced by PS Japan Corp.) was used as the HIPS, and decabromodiphenylether (produced by Wako Pure Chemical Industries, Ltd.) was used as the brominated flame retardant. As the sample piece 1, the brominated flame retardant was added to and kneaded with the HIPS so that the concentration becomes above each value; thus, pellets were prepared in which the size of the single pellet is 5 mm × 3 mm × 3mm, and the weight is approximately 0.3 g. Similarly to the procedure represented in Fig. 2, the single HIPS pellet as the sample piece 1 was mounted in contact with a silver substrate as the sample table 2, a mixed solvent of toluene and methanol (toluene/methanol = 1/1 by volume) as the extraction solvent 3 of 20 μl was dropped, using the microcyringe 4, close to the HIPS pellet, so as to inject the mixed solvent into the gaps between the HIPS pellet and the silver substrate, and then, the sample piece was kept. This mixed solvent is a solvent for extracting not only the HIPS but also the brominated flame retardant. Then, after 30 seconds passed from the drop operation, the HIPS pellet was removed from the silver substrate, nitrogen gas was blown onto the surface of the silver substrate on which the HIPS pellet was removed, and the solvent containing the brominated flame retardant was dried; thus, extract was deposited on the surface of the silver substrate. The processing time was approximately one minute from this mixed solvent being dropped until the extract was deposited onto the surface of the silver substrate. The grades of toluene and methanol used in this example were the liquid chromatographic ones (produced by Wako Pure Chemical Industries, Ltd.).

In this example, the deposited substance on the surface of the substrate was analyzed by the time-of-flight secondary ion mass spectrometry method. TRIFT2™ (manufactured by ULVAC-PHI Inc.) was used as the time-of-flight secondary ion mass spectrometry analyzer. Regarding the measurement condition, $^{69}Ga^{+}$ ion was used as

the primary ion, the measurement mode of the secondary ion was set to the positive ion mode, the measurement range was set to m/z = 1 - 1500, and the mass resolution was set to approximately $\Delta M/M$ = 5000. Fig. 16 is, as an example of the measurement results, a mass spectrum of the extract extracted from the HIPS pellet including the brominated flame retardant of 0.1%. As represented in Fig. 16, the mass-spectrum peak caused by the peak B^+ due to the fragment of decabromodiphenylether as the brominated flame retardant and the peak Ag^+ due to the fragment of silver was observed at m/z = 1068. Quantitative analysis was performed using the normalized ($^{1068}(B+Ag)^+/^{107}Ag^+$) peak-area ratio in which the area of the peak at m/z = 1068 ($^{1068}(B+Ag)^+$) is normalized by the area of the peak at m/z = 107 ($^{107}Ag^+$). The above area ratio of the extract extracted from the HIPS pellet including the brominated flame retardant of 0.1% was 0.005.

Fig. 17 is a graph representing a relationship between the mass-spectrum peak-area ratios ($^{1068}(B+Ag)^+/^{107}Ag^+$) obtained from the analysis of the extracts being extracted from the HIPS pellets each including the brominated flame retardant of 0.1%, 1%, or 10% as the concentration, and the brominated flame retardant concentrations. An excellent linear relationship was obtained between the brominated flame retardant concentrations and the peak-area ratios. In this example, the processing time was 1 minute for extracting the brominated flame retardant as the content from the HIPS pellet; thus, it was determined that the quantitative analysis, up to also the minute concentration, of the brominated flame retardant as the content can be performed by an extremely short-time extraction operation. As described above, in the analyzing method according to this example, the extraction processing time can be considerably shortened compared to that in the conventional method, and a content included in a matrix that is soluble in a solvent extracting the content, such as the brominated flame retardant included in the HIPS specimen, can also be rapidly analyzed.

Example 7.

In this example, similarly to the method in Example 4, an HDPE pellet

including the antioxidant of 500 ppm by weight was prepared. This HDPE pellet as the sample piece 1 was mounted in contact with a silicon substrate as the sample table 2; then, similarly to the method in Example 4, after chloroform as the extraction solvent 3 was dropped and injected into the gaps between the HDPE pellet and the silicon substrate, the sample piece was kept. Then, by processing for 12 minutes similarly to the procedure in Example 4, the antioxidant was extracted into the solvent, and this antioxidant as the extract was deposited as a condensed substance onto the surface of the substrate. Fig. 18 is a view representing a state in which the content is extracted from the sample piece according to this example. As represented in Fig. 18, a support 43 is placed inside a washing bath 42, into which ion exchanged water is put, of an ultrasonic washer 41, and a silicon substrate 12 is mounted on the support 43. An HDPE pellet 11 is mounted in contact with the top face of this silicon substrate 12, and chloroform 13 is maintained in the gaps between the top face of the silicon substrate 12 and the HDPE pellet 11. Thus, in this example, during extraction processing, ultrasonic vibration, for example, at a frequency of 45 kHz, is added to the HDPE pellet 11, the chloroform 13, and the silicon substrate 12. The ultrasonic washer used in this example is Branson-Series Type 2510J-DTA™ (manufactured by Yamato Scientific Co., Ltd.).

Similarly to the method in Example 4, the deposited substance was analyzed by the time-of-flight secondary ion mass spectrometry method. Fig. 19 is a mass spectrum of the extract, obtained by the method according to this example, extracted from the HDPE pellet including the antioxidant of 500 ppm. As represented in Fig. 19, the mass peak due to the fragment of the antioxidant was observed at m/z = 775. The normalized ($^{775}M^+/^{28}Si^+$) area ratio in which the area of the peak at m/z = 775 ($^{775}M^+$) is normalized by the area of the peak at m/z = 28 ($^{28}Si^+$) caused by the fragment of silicon in the substrate was 25, which is five times larger than that of Example 4 in which the ultrasonic waves were not added during the extraction operation. That is, by adding the ultrasonic waves, the extract amount of the antioxidant was increased. In the method according to this example, because the extract amount of the content is increased, in response to a material in which the amount of content to be analyzed is

further minute, the content can also be accurately analyzed in a short time.

Embodiment 8.

In this example, similarly to the procedure in Example 5, a PP pellet as the sample piece 1 including the brominated flame retardant of 100 ppm by weight was prepared. This pellet was mounted in contact with a silver substrate as the sample table 2; then, similarly to the procedure in Example 5, after toluene as the extraction solvent 3 was dropped and injected into the gaps between the PP pellet and the silver substrate, the sample piece was held. The sample piece was kept for 10 minutes in a state in which the toluene is maintained in the gaps between the PP pellet and the silver substrate; thereby, the brominated flame retardant was extracted into the toluene, so that the brominated flame retardant as the deposited substance was deposited on to the silver substrate as a condensed substance. Fig.20 is a view representing a state according to this example, in which the content is extracted from the sample piece. As represented in Fig. 20, during the extraction operation, a silver substrate 22, on which a PP pellet 21 is mounted, and between which and the PP pellet 21 toluene 23 is maintained in the gaps, is placed inside a sealed container 51 in which toluene vapor is saturated. Specifically, toluene 52 that generates its vapor is contained at the bottom of this sealed container 51, and a shelf plate 53 having holes is provided on the upper side of the toluene 52 that generates its vapor. The silver substrate 22 is placed on the top face of this shelf plate 53, the PP pellet 21 is mounted in contact with the top face of this silver substrate 22, and the toluene 23 is maintained in the gaps between the top face of the silver substrate 22 and the PP pellet 21. That is, because the PP pellet 21 is stored in saturated vapor of the toluene during the operation in which the brominated flame retardant is extracted from the PP pellet 21, loss, due to vaporization, of the toluene 23 as the extraction solvent can be prevented; therefore, the re-dropping of the toluene 23 becomes unnecessary, and the analysis process becomes simple. After the extraction, the silver substrate was taken out from the sealed container 51, the PP pellet 21 was removed from the silver substrate 22, and the solvent was dried with nitrogen gas being blown onto the surface

of the silver substrate 22, so that the brominated flame retardant was deposited on the surface of the silver substrate 22 as a condensed substance.

In this example, similarly to the method in Example 5, the deposited substance on the surface of the substrate was analyzed by the time-of-flight secondary ion mass spectrometry method. Fig. 21 is a mass spectrum of the extract, obtained by the method according to this example, extracted from the PP pellet including the brominated flame retardant of 100 ppm. As represented in Fig. 21, a mass spectrum peak due to the fragment of the bromine element was observed at m/z = 79. Quantitative analysis of the brominated flame retardant included in the PP pellet could be performed using the normalized ($^{79}Br^-/^{107}Ag^-$) peak area ratio that is obtained from the area of the peak at m/z = 79 ($^{79}Br^-$) being normalized by the area of the peak at m/z = 107 ($^{107}Ag^-$) caused by the fragment of silver in the substrate. That is, in the method according to this example, not only the extraction processing time can be considerably shortened compared to that in the conventional method, but also the re-dropping of the extraction solvent becomes unnecessary; moreover, because of the simple process, the brominated flame retardant as the content included in the PP specimen can be rapidly analyzed.

Example 9.

In this example, similarly to the procedure in Example 6, an HIPS pellet including the brominated flame retardant of 0.1% by weight was prepared. In this example, except for a mixed solvent of toluene and methanol (toluene/methanol = 1/1 by volume) in which silver perchlorate is saturated being used as the extraction solvent 3, similarly to the procedure in Example 6, extract from the HIPS pellet was deposited as a condensed substance on the surface of the silver substrate.

In this example, similarly to the method in Example 6, the deposited substance on the surface of the substrate was analyzed by the time-of-flight secondary ion mass spectrometry method. Fig. 22 is a mass spectrum of the extract, obtained by the method according to this example, extracted from the HIPS pellet including the brominated flame retardant of 0.1%. As represented in Fig. 22, the mass spectrum

peak due to the fragments of decabromodiphenylether as brominated flame retardant and silver was observed at m/z = 1068. The normalized ($^{1068}(B+Ag)^+/^{107}Ag^+$) peak area ratio in which the area of the peak at m/z = 1068 ($^{1068}(B+Ag)^+$) is normalized by the area of the peak at m/z = 107 ($^{107}Ag^+$) caused by the fragment of silver in the substrate was 0.05, which is ten times larger than that of Example 6 in which silver perchlorate as a conductive substance is not added. That is, in the method according to this example, compared to the conventional method, not only the extraction processing time can be considerably shortened, but also the sensitivity for analyzing the extract is remarkably improved; consequently, the brominated flame retardant as the content included in the HIPS specimen can be rapidly analyzed.

INDUSTRIAL APPLICABILITY

The method of analyzing the minute quantity of the content according to the present invention can be used for analyzing a minute quantity of a content such as an additive included in a polymer material such as plastic, rubber, adhesives, encapsulating resin, or mold resin. Moreover, a minute quantity of a content included in a polymer material constituting an instrumental part such as a case, a molded product, and a printed wiring board that are manufactured using the polymer material can be analyzed.